Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes

Sabine Horn, Claudio Gandolfi, Martin Albrecht*

Kinetic modelling with direct B-to-7 transformation

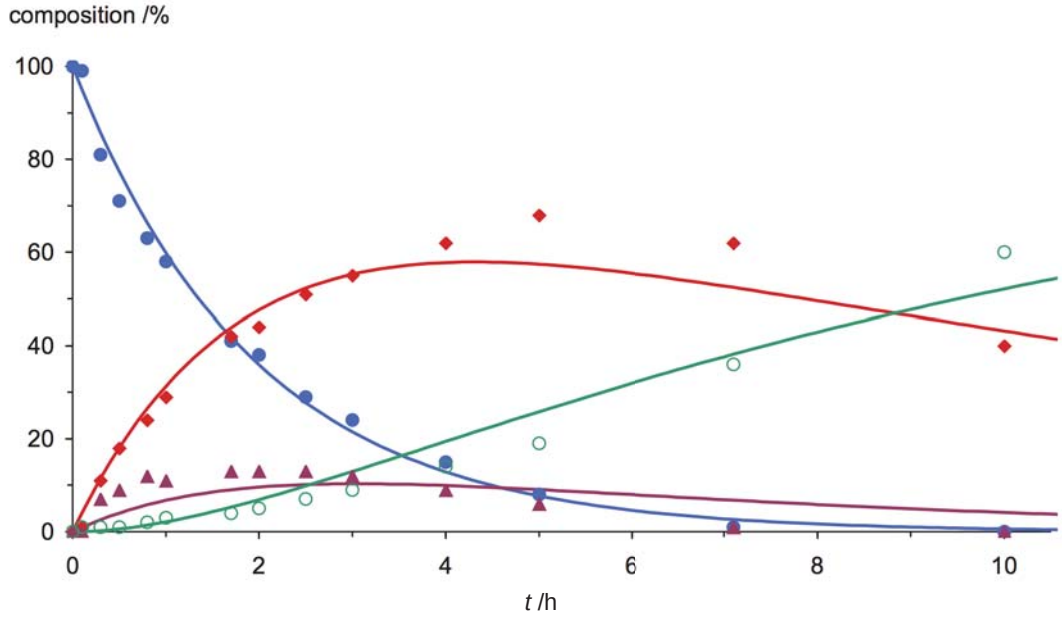

Figure S1. Time-dependent monitoring of the transfer hydrogenation of **6** (●) by GC-MS and evolution of products **A** (◆), **B** (▲), and **7** (O). Solid lines correspond to fitted rate constants using Berkeley Madonna upon suppressing isomerization between intermediates **A** and **B** (k_5 = 0 in Scheme 1) and implying a direct hydrogenation of the enol intermediate **B** to **7** instead ($k_4 \neq 0$). The fit provides a poor representation of the relative concentrations of **B** and a weaker convergence for **A** when compared with a fit including isomerization of **B** to **A** (*cf* Fig. 3). The modelled rate constants for this poorer fit are k_1 = 0.451, k_2 = 0.096, k_3 = 0.079, k_4 = 0.194, suggesting that C=C bond reduction in **6** is about five times slower than C=O bond reduction.

Crystallographic details.

Crystal data were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector using monochromated Mo-K_α radiation (0.71073 Å). A twice redundant dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed.[S1] The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[S2] Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic thermal

displacement parameters were used for all non-hydrogen atoms. Further crystallographic details are compiled in Table S1. CCDC 810172 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for complex **5**

crystal size	0.175 × 0.056 × 0.017 mm^3
Empirical formula	$C_{17}H_{26}Cl_2N_2Ru \times 0.5\ CH_2Cl_2$
Fw	945.66
T	100(2) K
crystal system	Monoclinic
space group	*P*–1 (no. 2)
unit cell	a = 10.3524(4) Å α = 111.427(4)°
	b = 13.0811(5) Å β = 94.023(3)°
	c = 16.5139(7) Å γ = 103.646(4)°
Volume	1992.55(16) $Å^3$
Z	2
D_{calcd}	1.576 g cm^{-3}
μ	1.191 mm^{-1}
no. total, unique reflcns	34740, 8161
R_{int}	0.0476
transmission range	0.874–0.981
no. parameters, restraints	434, 0
GOF	1.031
R, I > 2σ(I)	R_1 = 0.0274, wR_2 = 0.0535
R, all data	R_1 = 0.0398, wR_2 = 0.0586
largest diff. peak, hole	0.430, –0.471 e $Å^{-3}$

[S1] Program CrysalisPro Version 1.171.33.55, Oxford Diffraction Limited, 2010.

[S2] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

Datablock complex5 - ellipsoid plot